Isobaric Vapor-Liquid and Vapor-Liquid-Liquid Equilibrium for the Water + Ethanol + n-Hexane System

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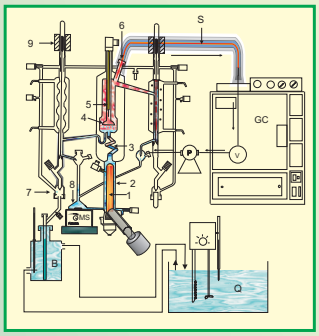
Heterogeneous azeotropic distillation is a widely used technique for separating binary azeotropic mixtures into their components. For many years, the traditional process to obtain pure ethanol from a water - ethanol mixture has been heterogeneous azeotropic distillation using benzene as the entrainer. In the last few years, because of the carcinogenic effect of benzene, this entrainer has been substituted by other compounds.

The absolute ethanol produced with this process can be used as a carburant mixed with gasoline. Since n-hexane is a common compound found in gasoline and is suitable for use it as an entrainer in the azeotropic distillation of ethanol, any remaining amount of hexane in the anhydrous ethanol will not be a problem for its subsequent use as a fuel.

However, it is not possible to find a complete experimental study in literature of the isobaric vapor-liquid-liquid equilibrium (VLLE) and vapor-liquid equilibrium (VLE) of the water - ethanol - n-hexane system at atmospheric pressure in literature. Usually, the equilibrium data for this system, which are necessary for the design and simulation of the heterogeneous azeotropic distillation process are substituted by predictions of these data using activity coefficient models as group contribution models like UNIFAC or by the UNIQUAC or NRTL model with parameters based on the correlation of binary VLE and LLE data.



1. Immersion heater
2. Boiling Flask
3. Cotrell pump
4. Separation Chamber
5. Thermometer
6. Vapor sample take-off
7. Liquid sample take off
8. Mixing chamber
9. Solenoid valve

Equipment

The determination of vapor-liquid-liquid equilibrium data was carried out in an all-glass dynamic recirculation still with an ultrasonic homogenizer coupled to the boiling flask. The use of ultrasonic sound on the boiling flask causes the emulsification of the two liquid phases throughout the still and thus prevents the oscillations in temperature and flow rate of systems with two liquid phases.

Analysis

The analysis of the equilibrium phases was carried out by gas chromatography, except for water in the organic phase, which was determined by the Karl Fischer method. The vapor phase was analyzed without prior condensation to prevent phase split. For the sampling of the liquid phases, a heterogeneous dispersed sample was placed in a tube where it splits into two liquid layers at their bubble point. Samples of each layer were taken later to be analyzed.

Results

Figure 1 shows the presence of a ternary azeotrope in the heterogeneous region.

The composition of the ternary azeotrope determined by numerical interpolation is 0.105, 0.236 and 0.658 mole fraction of water, ethanol, and n-hexane, respectively, and the temperature is 329.21 K.

In figure 3 can be seen that the models properly correlate the experimental data, except the top of the non-isothermal binodal curve.

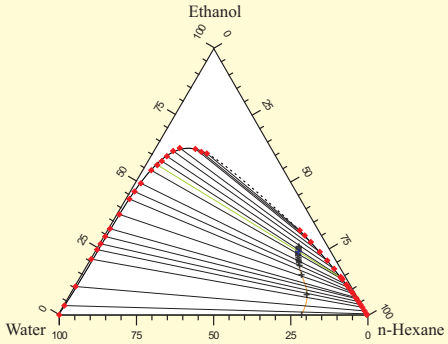


Figure 1. VLLE data (mol %), including the non-isothermal binodal curve and the vapor line.

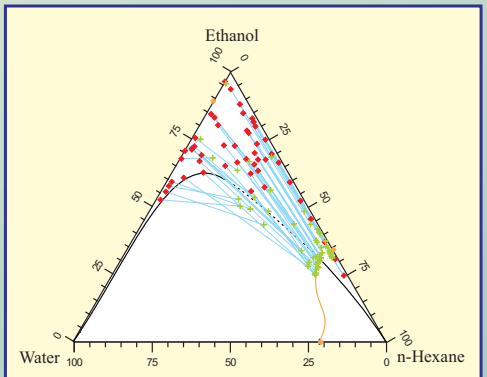


Figure 2. VLE data (mol %) of liquid mixtures in the homogeneous region of this multicomponent system.

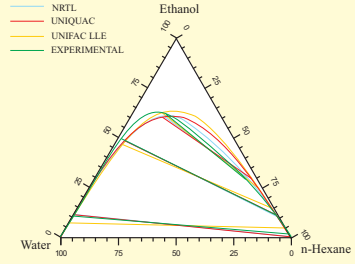


Figure 3. Comparison of the non-isothermal binodal curve and some tie lines calculated with UNIFAC LLE and with the parameters obtained with NRTL and UNIQUAC.

Conclusions

From the point of view of the use of these systems in the dehydration of ethanol using an azeotropic distillation column, the efficiency of the process is improved when the amount of water eliminated in the condenser-decanter of the column is greater.

As the vapor leaving the top of the column has a composition closed to the azeotropic one, the composition of the aqueous phase of the tie line containing this point is related with the amount of water that can be eliminated after condensation and decantation.

As can be seen in Figure 4, the water content in the aqueous phase in the system with benzene is greater than in those with cyclohexane and n-hexane. For these two systems, it is necessary to recirculate a greater amount of all the components to separate the same amount of water with the consequent increase in the production cost.

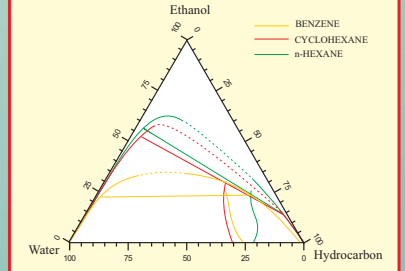


Figure 4. Comparison of the non-isothermal binodal curve, the vapor line and the tie line containing the azeotropic point for each one of the water-ethanol-hydrocarbon system